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(71) Applicant 000002886

Dainippon Ink & Chem. Inc.

3-35-58 Sakashita, Itabashi-ku, Tokyo

(72) Inventor

Tamaki Nakai

D-910, 21 Katakiriyama, Suita City, Osaka Prefecture

(74) Representative 100088764

Shori Takahashi, Patent Attorney

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(54) [Title of the Invention]

Resin Composition and Resin Molding Process

(57) [Abstract]

[Problem to Be Solved]

Thermoplastic polyester resins such as PET, etc., for molding show marked adhesion on the metal surface at the time of melting by heating. Consequently, the adhesion of resins to plasticization cylinder and molding mold of molding machine or calendering rollers is a problem.

[Solution]

Thermoplastic polyester resins are prevented from adhering to the metal surface by compounding with a polyolefin resin having a styrene-type side chain graft-polymerized and/or montanic acid wax. Consequently, it becomes possible to improve the yield at the time of extrusion, shorten the time required for cleaning plasticization cylinder, etc., of molding machine and carry out calendering of PET films and sheets.

[Patent Claims]

[Claim 1]

A thermoplastic polyester resin composition characterized by containing a polyolefin resin having a monomer different from the monomer of the main chain graft-polymerized as a side chain and/or montanic acid wax.

[Claim 2]

The resin composition of Claim 1, wherein the graft-polymerized polyolefin is a single resin or mixture of resins selected from low-density polyethylene with polystyrene graft-polymerized, low-density polyethylene with poly(methyl methacrylate) graft-polymerized, low-density polyethylene with a polyacrylonitrile-styrene copolymer graft-polymerized, polypropylene with polystyrene graft-polymerized, polypropylene with poly(methyl methacrylate) graft-polymerized and polypropylene with a polyacrylonitrile-styrene copolymer graft-polymerized.

[Claim 3]

The resin composition of Claim 1 or 2, wherein the thermoplastic polyester is a single resin or mixture of multiple resins selected from polyethylene terephthalate, non-crystalline polyethylene terephthalate resin, which is a copolymer of polyethylene terephthalate and polybutylene terephthalate.

[Claim 4]

A process for molding of thermoplastic polyester characterized by being a process for molding of a resin composition containing thermoplastic polyester and using a resin composition containing a polyolefin resin having a monomer different from the monomer of the main chain graft-polymerized as a side chain and/or montanic acid wax.

[Claim 5]

The process for molding of Claim 4, wherein the graft-polymerized polyolefin is that of Claim 2.

[Claim 6]

The process for molding of Claim 4 or 5, wherein the molding is calendering.

[Detailed Explanation of the Invention]

[0001]

[Technical Field of the Invention]

This invention allows to reduce the adhesiveness of thermoplastic resins, which show marked adhesion on the metal surface of processing machines at the time of melting by heating improving the workability and making cleaning after processing easy. Especially, it enables calendering of non-crystalline polyethylene terephthalate resins showing strong melt adhesion to be carried out without any problem.

[0002]

[Prior Art]

Polyethylene terephthalate (called PET, below), which is a typical thermoplastic polyester resin, is molded by heating and melting. In the case of this molding, the molten resin is liable to show severe adhesion to the metal surface of molding machines, consequently, the fluidity in the case of extrusion molding is very poor, and it is difficult to improve the yield. Furthermore, in the case of cleaning of the machines after use, the peelability of the resin adhered is poor, and consequently, it is necessary to feed a large quantity of a cleaning resin for a long period of time. Especially, the melt adhesiveness of non-crystalline or amorphous polyethylene terephthalate resin (called A-PET, below), which is a copolymer, is strong, and the molding is extremely difficult. In the case of A-PET, there are strong demands for films and sheets produced by calendering in recent years, but the adhesion to calender rollers is severe, and consequently, it has been practically impossible to carry out calendering. To eliminate this problem, the use of various lubricants has been proposed, but no ideal lubricant has been found to date.

[0003]

[Object of the Invention]

Therefore, the object of this invention is to provide a process enabling workability to be improved and calendering to be carried out by reducing the melt adhesiveness of PET, A-PET, etc.

[0004]

[Means to Accomplish the Object]

Namely, the inventor of this invention studied diligently, as a result, he found that the inventions shown in the patent claims were effective for accomplishing the above object. Specifically, the inventions are as follows.

[0005]

The invention of Claim 1 is a thermoplastic polyester resin composition characterized by containing a polyolefin resin having a monomer different from the monomer of the main chain graft-polymerized as a side chain and/or montanic acid wax.

[0006]

The invention of Claim 2 is the resin composition of Claim 1, wherein the graft-polymerized polyolefin is a single resin or mixture of resins selected from low-density polyethylene with polystyrene graft-polymerized, low-density polyethylene with poly(methyl methacrylate) graft-polymerized, low-density polyethylene with a polyacrylonitrile-styrene copolymer graft-polymerized, polypropylene with polystyrene graft-polymerized, polypropylene with poly(methyl methacrylate) graft-polymerized and polypropylene with a polyacrylonitrile-styrene copolymer graft-polymerized.

[0007]

The invention of Claim 3 is the resin composition of Claim 1 or 2, wherein the thermoplastic polyester is a single resin or mixture of multiple resins selected from polyethylene terephthalate, non-crystalline polyethylene terephthalate resin, which is a copolymer of polyethylene terephthalate and polybutylene terephthalate.

[0008]

The invention of Claim 4 is a process for molding of thermoplastic polyester characterized by being a process for molding of a resin composition containing thermoplastic polyester and using a resin composition containing a polyolefin resin having a monomer different from the monomer of the main chain graft-polymerized as a side chain and/or montanic acid wax.

[0009]

The invention of Claim 5 is the process for molding of Claim 4, wherein the graft-polymerized polyolefin is that of Claim 2.

[0010]

The invention of Claim 6 is the process for molding of Claim 4 or 5, wherein the molding is calendering.

[0011]

The inventions described above may be summarized to a single sentence that this invention pertains to a method for reducing the melt adhesiveness of thermoplastic polyester resins by allowing them to contain a graft-polymerized polyolefin resin and/or montanic acid wax.

[0012]

[Preferred Embodiment of the Invention]

Typical examples of preferred embodiment of this invention and optimal conditions are specifically shown in those application examples described later, but those constituting elements required and selectable to carry out this invention are explained in detail as follows.

[0013]

As a polyolefin resin having a monomer different from that of the main chain graft-polymerized as a side chain (called grafted polyolefin resin, below), there are, for example, low-density polyethylene with polystyrene graft-polymerized, low-density polyethylene with poly(methyl methacrylate) graft-polymerized (called LDPE-g-PMMA, below), low-density polyethylene with a polyacrylonitrile-styrene copolymer graft-polymerized (called LDPE-g-AS, below), polypropylene with polystyrene graft-polymerized, polypropylene with poly(methyl methacrylate) graft-polymerized and polypropylene with a polyacrylonitrile-styrene copolymer graft-polymerized. They are used alone or as a mixture of multiple kinds by kneading into thermoplastic polyester resins reducing the adhesiveness of thermoplastic polyester resins at the time of thermal melting. LDPE-g-PMMA and LDPE-g-AS are especially useful because the compatibility with thermoplastic polyester resins is good, and the melt adhesiveness-reducing effects are excellent.

[0014]

Specific examples of montanic acid wax are commercially available montanic acid itself, montanate wax and partially oxidized montanate wax, and they are all effective.

[0015]

Both grafted polyolefin and montanic acid wax are effective for reducing the melt adhesiveness of thermoplastic polyester resins by using alone, but they are preferably used concomitantly. Montanic acid wax has been used conventionally as a lubricant previously, and if it is added to thermoplastic polyester resins, it also works as a lubricant delaying the gelation time of polyester, but if it is used concomitantly with the grafted polyolefin resin, the gelation time delay of polyester can be shortened.

[0016]

Furthermore, with respect to the grafted polyolefin resin, the melt adhesiveness of thermoplastic polyester resins can be reduced by reducing the amount of the grafted polyolefin resins. As a result of a synergistic effect of the two components, their amounts to be added can be reduced, and consequently, it is possible to reduce the effects on the physical properties of thermoplastic polyester resins effectively.

[0017]

The amount of the grafted polyolefin resin and/or montanic acid wax to be added is not especially limited, and it is suitably set within the range wherein the effects of this invention are exhibited, and the application purposes of thermoplastic polyester resins are not damaged.

[0018]

Specifically, it is suitably determined by considering the method of processing such as extrusion or calendering, degree of melt adhesiveness reduction required, gelation time delay allowed and effects on the physical properties of thermoplastic polyester resins. For example, the aim for the amount of addition is in the range of 1-10 parts by weight per 100 parts by weight of thermoplastic polyester.

[0019]

Any of those conventionally used methods is usable for adding the grafted polyester resin and/or montanic acid wax to thermoplastic polyester. Specifically, there are, for example, direct addition of the grafted polyester resin and/or montanic acid wax to thermoplastic polyester and subsequent kneading; addition of a master batch, which is prepared by adding a high concentration of the grafted polyester resin and/or montanic acid wax to a small amount of thermoplastic polyester, to the thermoplastic polyester and subsequent kneading; addition of a coloring agent containing the grafted polyester resin and/or montanic acid wax to thermoplastic polyester and subsequent kneading; etc.

[0020]

As a thermoplastic polyester resin, there are polybutylene terephthalate resins as well as PET and A-PET described above.

[0021]

The effects of the grafted polyester resin and/or montanic acid wax reducing the melt adhesiveness of thermoplastic resins are also effective in the case of polar thermoplastic resins such as thermoplastic polyurethane, Nylon resins such as Nylon 6, Nylon 66, etc.

[0022]

[Application Examples]

This invention is explained specifically in detail by using application and comparative examples as follows, but this invention is not necessarily limited to these application examples.

[0023]

As a method for confirming the effects of this invention reducing the adhesiveness of thermoplastic polyester resins at the time of melting by heating, the following method was used.



[0024]

In a Laboplast mill manufactured by Toyo Seiki K.K., a roller mixer (Model R-60) (volume: about 60 cc) was installed. The mixer was charged with a sample, which was a composition of resin, etc., used in an application or comparative example, and the kneading was carried out under a condition of the pressure device removed for 10 min. Subsequently, the mixer was immediately disassembled, the state of resin adhesion to various blocks forming the container portion of the mixer was inspected by naked eye. Furthermore, a metal spatula was used to peel off the kneaded mixture from respective blocks, and the ease of peeling was used to determine the extent of adhesiveness. Furthermore, the time of the torque during kneading to reach its peak was measured as a gelation time.

[0025]

As a thermoplastic polyester resin, Eastman Kodak Kodar PETG 6763 (called PETG, below), which is a A-PET resin showing marked adhesion at the time of melting, was used.

[0026]

To avoid any effect of hydrolysis due to moisture absorption by PETG, all samples used for the test were dried, in advance, in a hot-air dryer at 80°C for 3 hr or longer before testing.

[0027]

Specific materials used for those components of the compositions prepared were as follows.

LDPE-g-PMMA: Modiper A1200 manufactured by NOF Corp.

LDPE-g-AS: Modiper A1400 manufactured by NOF Corp.

Partially oxidized montanate wax: Hoechstwax OP manufactured by Clariant (Japan) K.K.

Polyethylene wax: Epolene N10 manufactured by Eastman Kodak (K.K.)

GX-6: fatty acid ester-type mold-releasing agent manufactured by Ipposha Yushi Kogyo (K.K.)

EP-525L: magnesium-zinc organic complex mold-releasing agent manufactured by Eishin Kasei (K.K.)

[0028]

Application Example 1-6 and Comparative Example 1-4

The components, thermoplastic polyester, polyolefin resin graft-polymerized and/or montanic acid wax, other wax, mold-releasing agent, etc., of the compositions shown in Table 1 and 2 were mixed and kneaded in the mixer described above. Subsequently, the adhesiveness, etc., of the kneaded mixtures prepared were evaluated.

[0029]

Table 1 and Table 2 show the results on adhesion state observation and gelation time measurement carried out for those kneaded compositions. The word, cylinder block used in the tables is the cylinder portion of the mixer, and the end block is a portion blocking the end of the cylinder. The blade is a rotary blade to carry out rotational stirring inside the cylinder.

[0030]

The resin, PETG, which was completely impossible to be peeled off from various blocks of the mixer, became peelable after adding graft-polymerized polyolefin resin and/or montanic acid wax implying the melt adhesiveness of PETG in its molten state was reduced. Especially in the application example 6, 20 g of the composition was kneaded for 5 min by using double rollers heated at 195°C, and it was possible to roll out a sheet of about 150  $\mu\text{m}$  thick. Therefore, it was found to be possible to carry out the production of films or sheets of PETG by carrying out calendering.

[0031]

[Effects of the Invention]

According to this invention, the adhesiveness of thermoplastic polyester resins in their molten state by heating can be reduced not only improving the yield at the time of extrusion and shortening the cleaning time of machines used but also enabling calendering to be carried out.

[0032]

[Table 1]

	Application Example					
	1	2	3	4	5	6
PETG	50.0	50.0	50.0	50.0	50.0	50.0
LDPE-g-PMMA	0.5					
LDPE-g-AS		0.05	0.5		0.15	1.0
Montanic acid wax				0.5	0.1	0.5
End block						
Adhesion	Yes	Yes	Yes	Yes	No	No
Peeling ease	Easy	Difficult	Easy	Easy and clean		
Cylinder block						
Adhesion	Yes	Yes	Yes	Yes	No	No
Peeling ease	Easy	Difficult	Easy but partly difficult	Easy and clean		
Blade						
Adhesion	Yes	Yes	Yes	Yes	Yes	Yes
Peeling ease	Easy and clean	Difficult	Easy but partly difficult	Easy and clean	Easy	Easy and clean
Gelation time	35 sec	23 sec	26 sec	3 min	57 sec	1 min 48 sec

[0033]

[Table 2]

	Comparative Example			
	1	2	3	4
PETG	50.0	50.0	50.0	50.0
Polyethylene wax		0.5		
EP-525 L			0.5	
GX-6				0.5
End block				
Adhesion	Yes	No	Yes	Yes
Peeling ease	Impossible	Impossible	Difficult	Impossible
Cylinder block				
Adhesion	Yes	Yes	Yes	Yes
Peeling ease	Impossible	Impossible	Impossible	Impossible
Blade				
Adhesion	Yes	Yes	Yes	Yes
Peeling ease	Impossible	Impossible	Difficult and partially impossible	Impossible
Gelation time	20 sec	*	1 min 37 sec	1 min

\* No gelation, stuck on the blade and impossible to mix uniformly.